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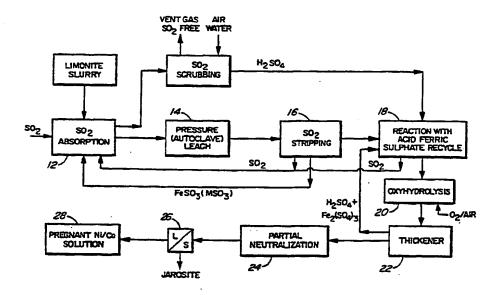
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(54) Title: PROCESS FOR EXTRACTION OF NICKEL AND COBALT FROM LATERITE ORES



#### (57) Abstract

A process for the extraction of nickel and cobalt from a laterite ore comprises the step of reacting the ore, in slurry form, with sulphur dioxide to convert the iron, nickel and cobalt in the ore to soluble sulphates and bisulphites in a product slurry. In a specific embodiment of the process, the product slurry is further treated to convert the bisulphites to sulphates and to precipitate iron as jarosite. An essentially iron free solution of nickel and cobalt is produced from which nickel and cobalt can be recovered by one or a combination of known methods.

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# PROCESS FOR EXTRACTION OF NICKEL AND COBALT FROM LATERITE ORES

#### FIELD OF THE INVENTION

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This invention relates to a process for extracting nickel and cobalt from laterite ores.

#### BACKGROUND OF THE INVENTION

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A high proportion of known world resources of nickel and cobalt are contained in laterite deposits. These deposits are typically derived from weathering of mainly magnesium silicate minerals, such as garnierite, which contain nickel and cobalt, as well as iron, aluminum, chromium and a wide range of trace elements.

Geologically, a profile of a fully developed laterite deposit comprises a high iron surface layer (ferricrete) with low nickel and cobalt content; a layer of limonite containing mainly iron oxides, typically more than 40% Fe dry basis, plus nickel-cobalt values; a layer of saprolite, which contains partially weathered magnesium silicate minerals, enriched in nickel and cobalt; fractured but largely weathered garnierite; and basement unweathered garnierite.

The present invention relates mainly to the limonite portion of lateritic nickel-cobalt deposits. However, the saprolite and weathered garnierite zones of suitable deposits may be used to advantage within the process.

There are process energy cost advantages

inherent to processes which treat lat rites by direct leaching, as opposed to roasting, which is a dry process

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taking place at high temperature, and which requires substantial energy input to evaporate the free and hydration water associated with typical laterite ores.

The principal commercial method involving direct hydrometallurgical treatment of limonitic nickel-cobalt ores is that practised at the Moa Bay mine in Cuba. This process involves high temperature, i.e., greater than 400°F (200°C), sulphuric acid leaching of laterite. To operate the leach at a temperature greater than 400°F, high pressure reaction vessels are required to maintain the sulphuric acid-water leach solution in the liquid phase.

The main advantage of the present invention compared to previously disclosed methods arises from essentially complete dissolution of metal oxide components of limonite, i.e., iron, nickel and cobalt, at much lower temperatures, typically 180-212°F (80-100°C), where steam pressure is minimal.

#### SUMMARY OF THE INVENTION

According to the invention there is provided a

25 process for the extraction of nickel and cobalt from a
laterite ore comprising the steps of reacting the ore, in
slurry form, with sulphur dioxide to convert the iron,
nickel and cobalt in the ore to soluble sulphates and
bisulphites contained in a product slurry.

The laterite ore may first be treated to extract a limonite portion therefrom, which limonite portion is reacted with said sulphur dioxid .

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The step of reacting the ore with sulphur dioxide may comprise a first stage SO<sub>2</sub> absorption in which a slurry of the ore and water is contacted with a mixture of SO<sub>2</sub> and N<sub>2</sub> such as from combustion of sulphur or sulphide minerals in air, followed by a second stage SO<sub>2</sub> absorption in which the slurry from the first stage is contacted with substantially 100% SO<sub>2</sub> gas and a pressure leach stage in which the slurry from the second stage SO<sub>2</sub> absorption is subjected to an elevated temperature and pressure.

Further objects and advantages of the invention will become apparent from the description of a preferred embodiment of the invention below.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram of one embodiment of the process according to the invention.

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Figure 2 is a flow diagram of another embodiment of the process according to the invention.

Figures 3 to 5 are flow diagrams illustrating 25 an embodiment of the process in more detail.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

The process according to the invention will

first be described generally with reference to Figures 1

and 2 and then in somewhat more detail with reference to

Figures 3 to 5.

With reference to Figure 1, the process

35 comprises a SO<sub>2</sub> absorption step 12 in which a slurry of limonite nickel-cobalt ore and water is contacted with SO<sub>2</sub>

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at or below ambient temperature. The next step is a pressure leaching step 14 at a temperature of from 180° - 212°F (80 - 100°C) and a SO<sub>2</sub> partial pressure of 80-200 psig (550 - 1400 kPa (gauge)) to substantially completely dissolve the metallic oxide components of the limonite, such as iron, nickel, cobalt, magnesium and manganese, as the soluble sulphates and bisulphites, according to the following reaction:

10 2MO.OH + 3SO<sub>2</sub> (aq) 
$$\rightarrow$$
 MSO<sub>4</sub> (aq) + M(HSO<sub>3</sub>)<sub>2</sub> (aq), (1)

where M = Fe, Co, Ni.

- Magnesium, aluminum and other metallic oxides of limonite are similarly dissolved. These components are not oxidized or reduced so that they are also present as sulphates or bisulphites.
- After the pressurized leach 14, the leach slurry is released to near atmospheric pressure and heated in an atmospheric SO<sub>2</sub> stripping step 16, to decompose the metal bisulphites according to the following reaction:

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$$M(HSO_3)_2 (aq) \rightarrow MSO_3(s) + SO_2(q),$$
 (2)

where M represents a metal, such as Fe, Ni, Co, Mg and Mn. Advantageously, part of the insoluble metal sulphates formed in step 16 is recycled to the SO<sub>2</sub> absorption step 12 to facilitate the absorption by the following buffering reaction (but this step is optional):

$$FeSO_3(s) + SO_2(g) + H_2O \rightarrow Fe(HSO_3)_2 (aq).$$
 (3)

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After the SO<sub>2</sub> stripping step 16, the slurry is subjected to a reaction step 18 with an acid ferric sulphate recycle stream to maximize recovery of sulphur dioxide by leaching of insoluble sulphites:

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$$MSO_3(s) + H_2SO_4(aq) \rightarrow MSO_4(aq) + SO_2(g),$$
 (4)

where M represents a metal.

The slurry is then subjected to oxidation and hydrolysis (oxydrolysis) 20 to precipitate iron as jarosite with concurrent generation of free sulphuric acid and iron (III) sulphate:

15 3FeSO<sub>4</sub> (aq) + 3/4 O<sub>2</sub> 
$$\rightarrow$$
 HFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>(s) + H<sub>2</sub>SO<sub>4</sub>, (5)

$$H_2SO_4 + 2FeSO_4 + \frac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O.$$
 (6)

- The product of the oxyhydrolysis step 20 is
  20 passed to a thickener 22 and part of the acidic solution
  is recycled to effect the reaction step 18. If desired,
  the jarosite can be separated in an optional liquid/solid
  separation step at this stage for disposal or use.
- The balance of the oxydrolysis product is treated in a neutralization step 24 with acid neutralizing material, advantageously saprolite or garnierite containing nickel and cobalt, to precipitate remaining iron as jarosite:

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$$MgO + 3/4 O_2 + 3FeSO_4 (aq) \rightarrow HFe_3(SO_4)_2(OH)_6 + MgSO_4(aq),$$
 (7)

in which MgO represents active magnesia from the saprolite or garnierite. Other acid neutralizing materials, such as limestone or dolomite can also be used.

If the neutralization 24 is carried out in seawater or water containing significant amounts of a monovalent cation(s), jarosite precipitation is facilitated by, for example:

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NaCl (aq) + 3FeSO<sub>4</sub> (aq) + 3/4 O<sub>2</sub> 
$$\rightarrow$$
  
NaFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> + H<sub>2</sub>SO<sub>4</sub> (aq) + HCl (aq). (8)

The neutralization step 24 is followed by a liquid/solid separation 26, to separate the jarosite and to produce a pregnant solution containing nickel and cobalt ions in solution, as indicated at 28.

Nickel and cobalt may be recovered from the

solution 28 by one or a combination of known methods,
such as sulphide precipitation, liquid ion exchange, i.e.
solvent extraction and stripping or hydrous oxide and/or
carbonate precipitation, which may optimally be followed
by ammonia leaching and separate recovery of nickelcobalt salts or metals.

In a particular embodiment of the invention, the  $SO_2$  absorption step 12 is carried out in two stages 30 and 32, as shown in Figure 2. In this embodiment, the first stage 30 is carried out with an  $SO_2$  -  $N_2$  mixture typically generated by the burning of sulphur or roasting of sulphide minerals in air or oxygen enriched air. The second stage 32 is carried out with 100%  $SO_2$  recycled from the steam stripping step 16 and the reaction step 18.

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The gas from the first  $SO_2$  absorption stage 30 is subjected to a  $SO_2$  scrubbing step 33 to provide a gas which can b vented to atmosphere. During the scrubbing process the  $SO_2$  is converted to  $H_2SO_4$  which is used in the reaction step 18.

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The process will now be described in more detail, by way of example, with reference to Figures 3 to 5. Referring to Figure 3, laterite ore is transferred from a stockpile 34 or directly from a mine truck 36 to a dump pocket 38 where it is slurried, as shown at 40, with salt water or sea water, or fresh water to which a source of monovalent jarosite stabilizing cations is added. However, if fresh water is used, the source of jarosite stabilizer is advantageously added after the thickener 56, which will be referred to below.

The slurry is passed to a rotary scrubber 41. By means of a trommel screen 42 on the scrubber 41 and sieve bends and cyclone, the ore is separated into primary fines 44, typically 0.5 mm, which is the limonite fraction of the ore, and oversize 46, which is mainly saprolite, i.e., partially weathered, high magnesium material, which is conveyed to a stockpile 47. The primary fines 44 are passed by a secondary screen 48, where further oversize is separated and conveyed to the stockpile 47.

The secondary fines from the screen 48 go to a pump box 50 from where they are pumped by pump 52 to a cyclone 54 for further separation in fines and oversize. The fines from the overflow of the cyclone 54 are passed to the thickener 56. The oversize from the cyclone underflow pass by a tertiary screen 62 where oversize is separated which is passed to the jarosite precipitation step 92 for utilization. The fines from the screen 62 go to pump box 64 from where they are pumped by pump 66 to the thickener 56.

The fine slurry of limonite which is passed to

35 the thickener 56 is dilute and it is thicken d or

concentrated in the thickener 56 for pip line transfer to

an SO<sub>2</sub> absorption stage, as indicated at 58. The thickener overflow, i.e. seawater diluted by the fresh water content of the raw ore, is discarded, as shown at 60.

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In Figure 4, the limonite slurry from the thickener 56, again indicated at 58, is fed to a counter-current absorption tower 68 where it contacts  $SO_2$  from an  $SO_2/N_2$  mixture of about 20%  $SO_2$  and about 80%  $N_2$ , which is also fed to the tower 68, as indicated at 70.

From the tower 68, the slurry, now in equilibrium with the SO<sub>2</sub> gas, passes to a second countercurrent absorption tower 72 to which is fed essentially 100% SO<sub>2</sub> gas from the SO<sub>2</sub> stripping of reduction autoclave product which is a later stage in the process and which will be described below. The slurry now equilibrates with the 100% SO<sub>2</sub> gas in the tower 72.

Gas exhausting from the first countercurrent tower 68 has residual SO<sub>2</sub> which must be scrubbed out before the gas can be exhausted. The SO<sub>2</sub> is reacted with excess air in an iron sulphate solution a shown as 74, to generate sulphuric acid, leaving an SO<sub>2</sub> free vent gas.

The sulphuric acid produced is reacted with the FeSO<sub>3</sub> slurry from the SO<sub>2</sub> stripping step 80, which will be described below, for the optimization of SO<sub>2</sub> recovery.

From the tower 72, the limonite slurry, now saturated with SO<sub>2</sub> at or slightly above atmospheric pressure, passes to a reduction leach autoclave 76, where heat, such as in the form of steam, is supplied to accelerate or facilitat process reaction (1) above.

The autoclave 76 operates at 180-212°F (80-100C°) and up to 250 psig (1725 kPa (gauge)) pressure.

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The reduced slurry exiting the autoclave 76 is indicated at 78.

Figure 5 shows the reduced slurry 78 passing to a series of SO<sub>2</sub> strip tanks 80 operated at slightly above atmospheric pressure in which steam drives off dissolved and reactive SO<sub>2</sub>, e.g.,

$$Fe(HSO_3)_2$$
 (aq)  $\rightarrow$   $FeSO_3(s) + SO_2(g)$  (9)

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The essentially 100% SO<sub>2</sub> gas from the strip tanks 80 is cooled in a cooler (not shown) and recycled to the second absorption tower 72, as indicated at 82.

The stripped slurry passes to an oxydrolysis autoclave 84 in which reaction with oxygen produces jarosite essentially free of Ni and Co. The jarosite is filtered by a drum filter 86 and pumped, by pump 88 to a tailing pond as shown at 90.

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The acidic solution from the filtration is further treated with prepared finely crushed saprolite to eliminate iron in a secondary jarosite precipitation stage, according to reaction aquation (7) above, and as indicated at 92.

The product of the secondary precipitation stage 92 is passed to a mixing tank 94 and pumped by pump 96 to a drum filter 98 to separate the solids from the secondary separation 92, which solids are disposed of, as indicated at 100.

The liquid product from the filter 98 is the pregnant solution which is the product of the process containing the nickel and cobalt ions in solution and indicated at 102.

While only preferred embodiments of the invention have been described herein in detail, the invention is not limited thereby and modifications can be made within the scope of the attached claims.

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#### WHAT IS CLAIMED IS:

1. A process for the extraction of nickel and cobalt from a laterite ore comprising the step of reacting the ore, in slurry form, with sulphur dioxide to convert the iron, nickel and cobalt in the ore to soluble sulphates and bisulphites contained in a product slurry.

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2. The process according to claim 1, wherein the laterite ore is first treated to extract a limonite portion therefrom, which limonite portion is reacted with said sulphur dioxide.

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- 3. The process according to claim 2, wherein said treatment comprises producing a limonite slurry, which comprises said limonite portion and water, which limonite slurry is reacted with said sulphur dioxide to produce said product slurry containing said sulphates and bisulphites.
  - 4. The process according to claim 3, wherein said water comprises sea water.

- 5. The process according to claim 3, further comprising the step of adding a source of monovalent jarosite stabilizing cations to said product slurry.
- 30 6. The process according to claim 1, further comprising the step of heating said product slurry to decompose said bisulphites to produce insoluble metal sulphites and SO, gas.

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- 7. The process according to claim 6, further comprising the step of recycling said SO<sub>2</sub> gas for reaction with the ore.
- 5 8. The process according to claim 6, further comprising the step of reacting said soluble sulphates with oxygen or air to oxidize dissolved iron sulphate to jarosite with concurrent generation of a solution of sulphuric acid and iron III sulphate.

9. The process according to claim 8, further comprising the step of reacting said insoluble metal sulphites with sulphuric acid to produce soluble sulphates and SO<sub>2</sub> gas.

10. The process according to claim 9, further comprising the step of recycling said SO<sub>2</sub> gas for a reaction with said ore.

20 11. The process according to claim 9 wherein the reaction of said insoluble metal sulphites with sulphuric acid is effected with a part of the solution of sulphuric acid and iron III sulphate from said iron sulphate oxidation to jarosite.

12. The process according to claim 8, further comprising the step of reacting said solution of sulphuric acid and iron III sulphate with a base to precipitate iron as jarosite and producing a solution of nickel and cobalt sulphates.

13. The process according to claim 12, wherein said base comprises a high magnesium fraction of laterite nickel deposit.

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14. The process according to claim 13, wherein said base comprises saprolite.

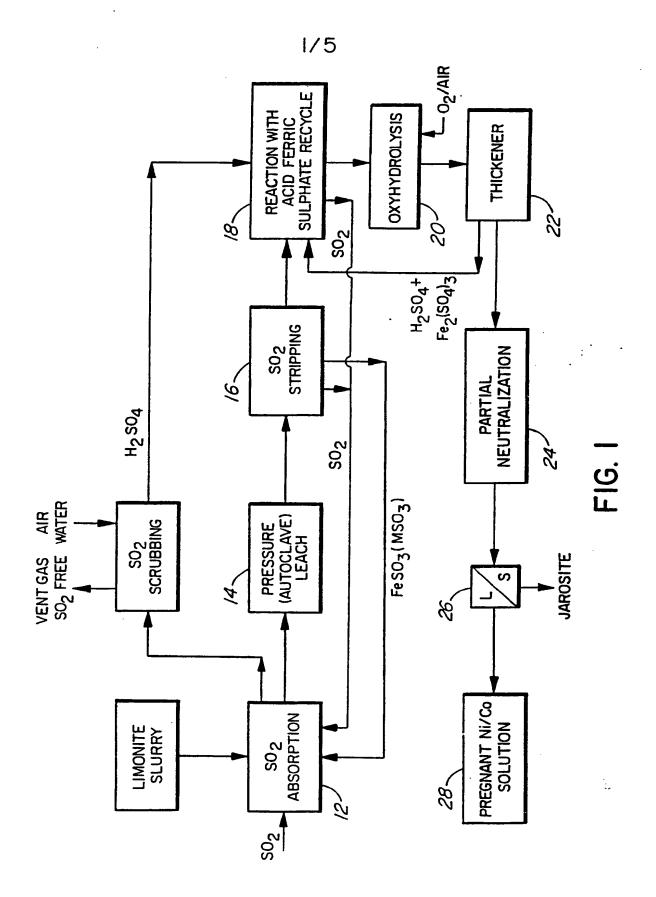
- 15. The process according to claim 14, wherein said base comprises garnierite.
  - 16. The process according to claim 13, wherein said base further comprises a reactive mineral carbonate.
- 10 17. The process according to claim 16, wherein said reactive mineral carbonate is selected from the group consisting of calcite, dolomite, magnesite and ankerite.
- 18. The process according to claim 1, wherein said step of reacting the ore, in slurry form, with sulphur dioxide comprises a first stage SO<sub>2</sub> absorption in which a slurry of the ore and water is contacted with a mixture of SO<sub>2</sub> and N<sub>2</sub>, a second stage SO<sub>2</sub>
- absorption in which the slurry from the first stage is contacted with substantially 100% SO<sub>2</sub> gas and a pressure leach stage in which the slurry from the second stage SO<sub>2</sub> absorption is subjected to an elevated temperature and pressure.
  - 19. The process according to claim 18, in which the elevated temperature is from about 180° to about 212°F and the pressure is a SO<sub>2</sub> partial pressure of from about 80 to about 200 psig.
  - 20. The process according to claim 18, further comprising the step of heating said product slurry to decompose said bisulphites to produce insoluble metal sulphites and SO<sub>2</sub> gas.

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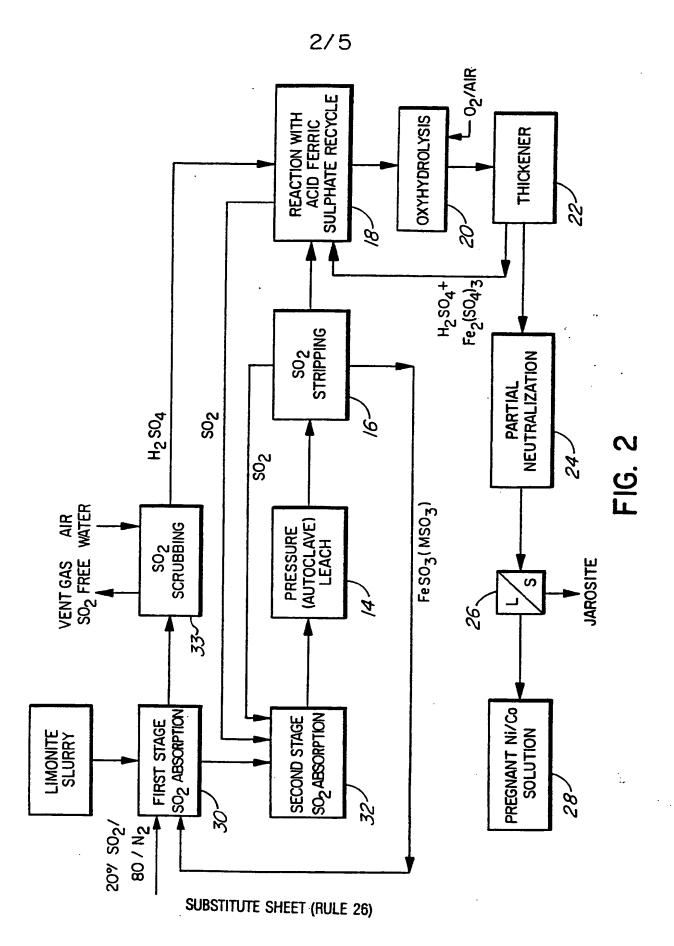
- 21. The process according to claim 20, further comprising the step of recycling said SO<sub>2</sub> gas to said second stage SO<sub>2</sub> absorption.
- 5 22. The process according to claim 20, further comprising the step of recycling part of said insoluble metal sulphites to said first stage SO<sub>2</sub> absorption.
- 10 23. The process according to claim 20, further comprising the step of reacting said soluble sulphates with oxygen or air to oxidize dissolved iron sulphate, thereby to precipitate jarosite with concurrent generation of a solution of sulphuric acid and iron III sulphate.
  - 24. The process according to claim 23, further comprising the step of reacting said insoluble metal sulphites with sulphuric acid to produce soluble sulphates and SO, gas.
  - 25. The process according to claim 24, further comprising the step of recycling said SO<sub>2</sub> gas to said second stage SO<sub>2</sub> absorption.

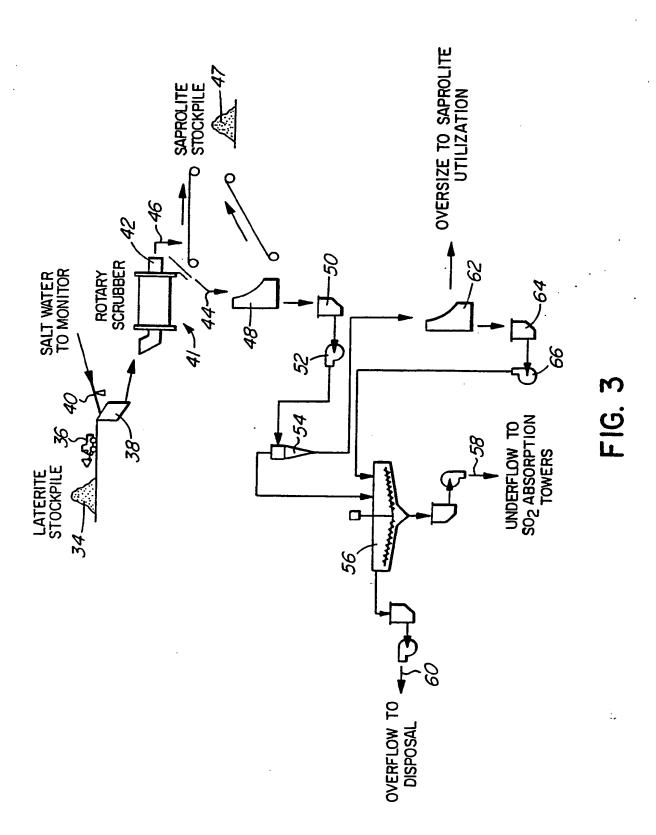
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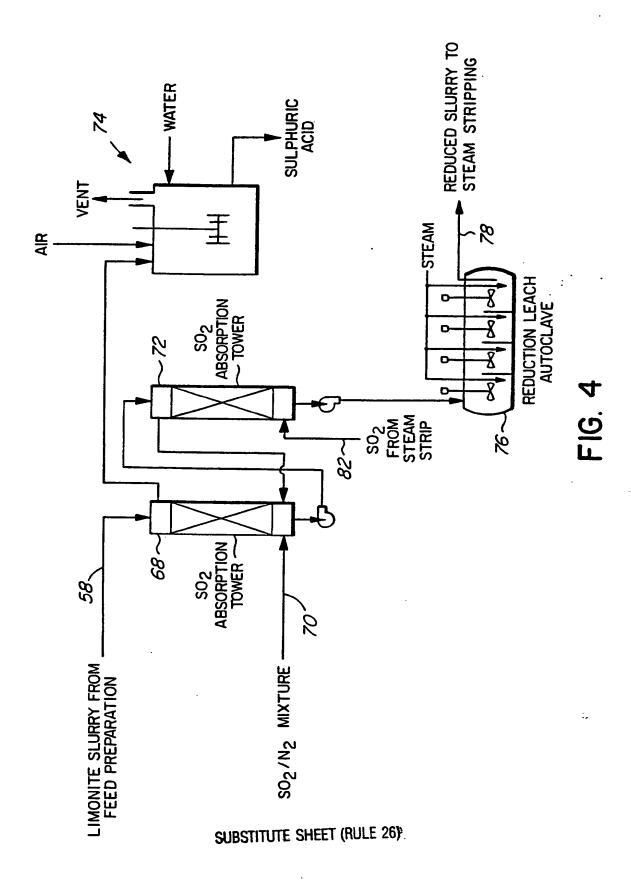


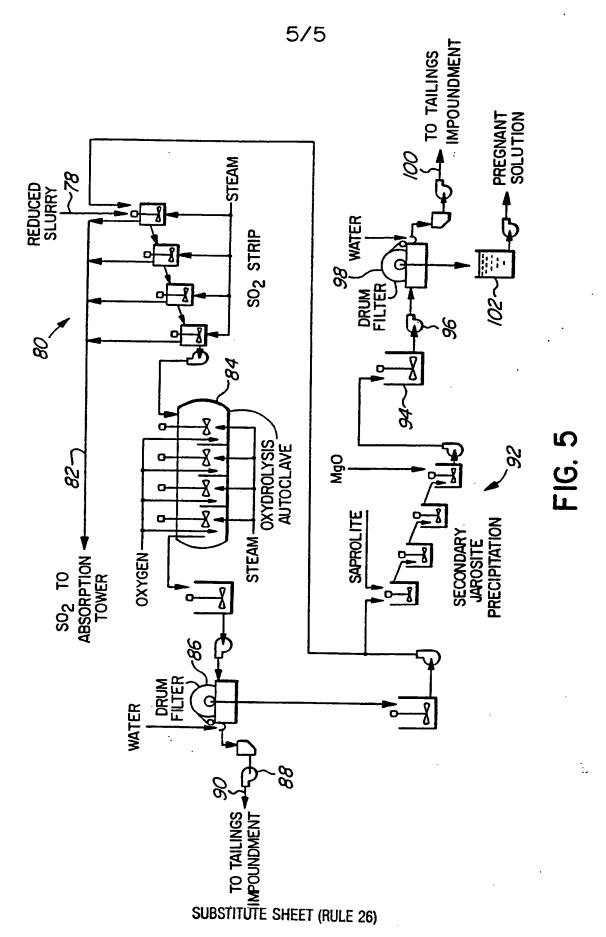
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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| C. DOCUM   | MENTS CONSIDERED TO BE RELEVANT   |                       |
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